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Effect of a Dipolar Self-Assembly Monolayer Formation on Indium-Tin Oxide on the Performance of Single-Layer Polymer-Based Light-Emitting Diodes

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Summary: We report on the use of indium-tin oxide surface modification, by grafting of highly polar *p*-disubstituted benzenes, in the fabrication of light-emitting diodes. The polar compounds possess COCl or SO_2Cl grafting groups and CF_3 or NO_2 as highly electronegative groups, leading to the formation of a dipolar monolayer, which brings about an increase in ITO work function, thereby reducing the barrier for hole injection into luminescent polymers. We observe that the effect of this self-assembled monolayer, in terms of light-onset voltage, efficiency and luminance, is at least comparable to the use of a hole injection layer of doped poly[(3,4-ethylenedioxy)thiophene] for LEDs using poly({2-[(2-ethylhexyl)oxy]-5-methoxy-1,4-phenylene}vinylene) (MEH-PPV) and polyfluorene blends as active layers.

Keywords: conjugated polymers; light-emitting diodes (LED); monolayers; polyfluorenes; self-assembly

Introduction

Electroluminescent (EL) polymers offer the prospect for the fabrication of cheap, flexible, large-area displays, among other potential applications. Light-emitting diodes (LEDs) are the key devices behind such an application, and a significant effort has been devoted to the optimization of their performance (efficiency, lifetime, colour stability). The control of charge injection and transport is of paramount importance, as these are fundamental processes in determining both the efficiency and the light-onset voltage of LEDs. More specifically, the

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improvement of hole injection from the anode side (usually indium-tin oxide, ITO), has involved the insertion of hole injection layers, such as doped polyaniline or poly[(3,4-ethylenedioxy)thiophene] doped with poly(styrenesulfonic acid), PEDOT:PSS[1], or graded hole-injection layers[2]. More recently, the possibility to chemically modify the ITO surface by grafting of polar organic compounds, as a means to increase its work function[3-5] or to increase its hydrophobicity[6], is attracting a significant interest. In particular, it was reported[5] that the work function of ITO could be tuned by grafting *p*-disubstituted benzene compounds, comprising a grafting group (SO_2Cl, COCl, or PO_2Cl_2) and an electron-attracting group, such as Cl or CF_3. We have recently reported on the effect of surface modification of ITO, by formation of such a dipolar self-assembled monolayer (SAM), on optoelectronic properties of LEDs based on poly({2-[(2-ethylhexyl)oxy]-5-methoxy-1,4-phenylene}vinylene) (MEH-PPV) where compounds with a stronger electron-attracting group, NO_2, were also used.[7] We now present the effect of similar ITO surface modifications on the optoelectronic characteristics of LEDs based on polyfluorenes, which are, presently, the most promising luminescent polymers for device applications.[2,8]

Figures 1 and 2 show the molecular structure of the polymers used in this study and of the polar compounds used in the formation of dipolar SAM onto ITO.

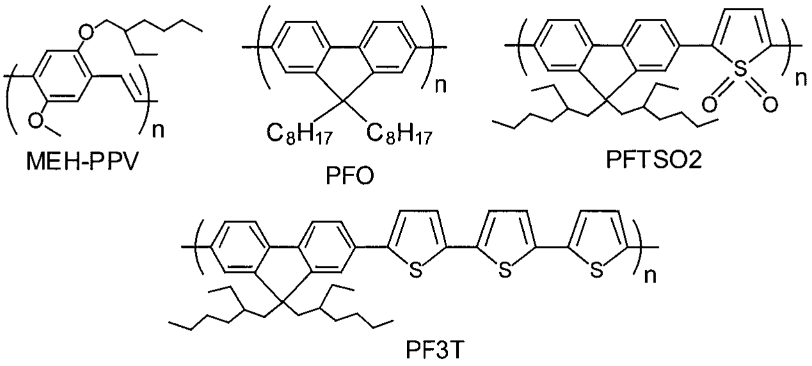

Figure 1. Molecular structure of the luminescent polymers.

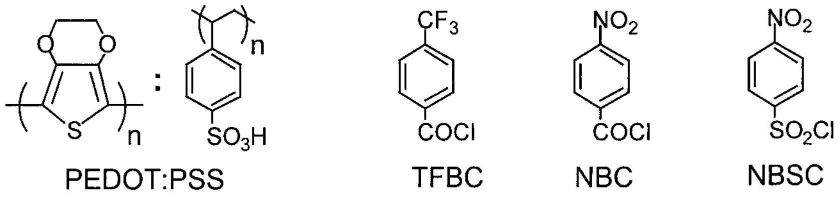

Figure 2. Molecular structure of PEDOT:PSS or PEDOT for short, used as hole-injecting material, and of the polar grafting compounds.

Experimental

MEH-PPV was synthesized by the Gilch route[9] and the copolymers PFTSO2 and PF3T were prepared by Suzuki coupling.[10] PEDOT:PSS was obtained from Bayer and the *p*-disubstituted benzenes were purchased from Aldrich. The SAM-modified ITO substrates were prepared by immersion for 5 min in dichloromethane solutions of the polar grafting compounds (1 mM), then washed with dichloromethane and dried under nitrogen flow. Reference LEDs were prepared using bare ITO substrates and ITO coated with PEDOT:PSS (55 nm thick). The fabrication of LED structures was completed by spin coating with the polymer or polymer blend solutions, followed by thermal evaporation of aluminum electrodes at a pressure of 10^{-3} Pa, defining pixel areas of 4 mm^2. MEH-PPV was used in the neat form, while the polyfluorenes were used as blends, namely, PFO:PF3T and PFO:PFTSO2, where the content of PFO, the host polymer matrix, was 95 % by weight.

Results and Discussion

Figure 3 shows the energetic positions of the relevant frontier levels of the polymers (PFO[11], PF3T[10], PFTSO2[10] and MEH-PPV[7]) and the work function of the electrodes. The ITO work function is considered to lie in the range 4.6-4.8 eV[12,13]; for PEDOT:PSS it is 5.2-5.3 eV.[13]

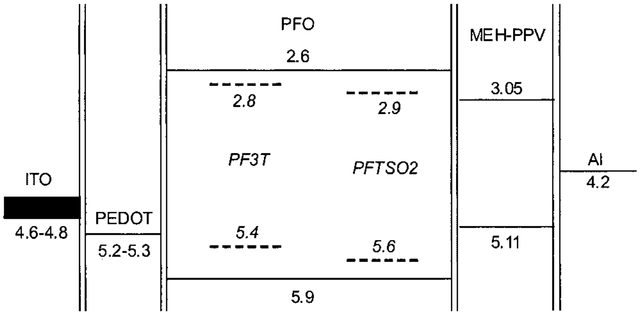

Figure 3. Energetic position of the frontier levels of various components used in fabrication of devices.

TFBC modification of ITO increases its work function by about 0.4 eV[5], which brings it to about 5.0-5.2 eV. Considering that the dipole moment of nitrobenzene is 4.22 D, much higher than the value of 2.86 D for (trifluoromethyl)benzene, we expect the work function of ITO-NBC to be higher than 5.0 eV. Based on the results obtained for chlorobenzene[5], we also expect the work function of ITO-NBSC to be slightly lower than that of ITO-NBC. Figure 4 compares the current and luminance for LEDs based on MEH-PPV. The SAM modification of ITO significantly reduces the light-onset voltage, though the maximum luminance is not significantly improved. Furthermore, the use of NBC or NBSC, which are expected to lead to a higher work function than TFBC, does not further reduce the light-onset voltage from the value of about 2.2 eV closer to 2.13 eV, the energy gap voltage. This result is in agreement with a work function of ca. 5.1 eV for ITO-TFBC, close to the highest occupied molecular orbital energy of MEH-PPV, and therefore corresponding to a negligible or no hole-injection barrier.

Figures 5 and 6 compare the optoelectronic characteristics of LEDs based on PFO:PF3T and PFO:PFTSO2 blends, where ITO was modified with NBSC. In both blends, there is an efficient energy transfer from the host PFO to the guest polymers[14]. The SAM modification of ITO significantly improves both the current density and the luminance of the LEDs in comparison with the use of bare ITO; they are similar or slightly higher than those of the LEDs with PEDOT. The EL efficiencies of the devices with ITO-NBSC anodes are similar to those based on ITO/PEDOT, being 0.05 – 0.09 % of external quantum efficiency.

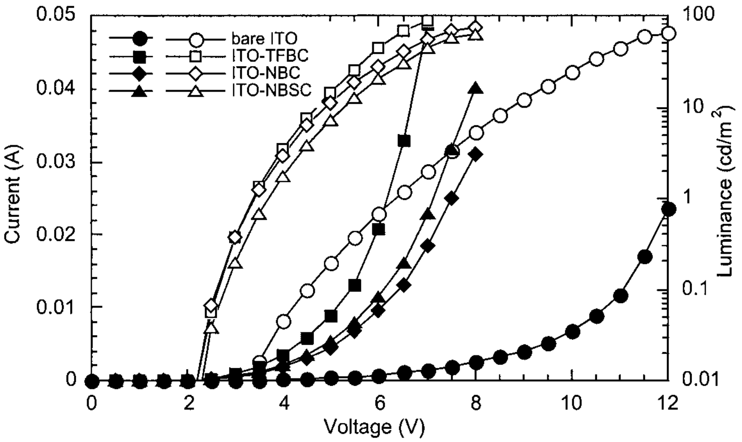

Figure 4. Current (filled symbols) and luminance as functions of the applied voltage for LEDs based on MEH-PPV (140 nm thick).

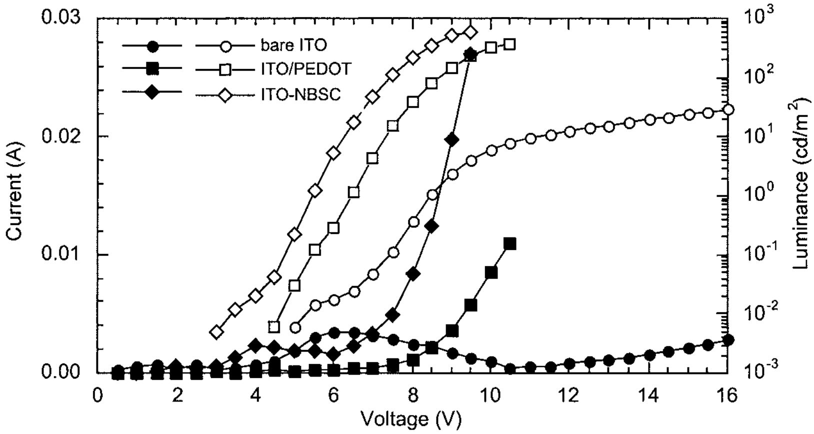

Figure 5. Current (filled symbols) and luminance of LEDs based on the PFO:PF3T blend (95 nm thick).

Conclusions

The SAM modification of ITO with NBSC allows the fabrication of LEDs based on polyfluorene blends with similar or even better performance (light-onset voltage, maximum luminance and EL efficiency) than that of LEDs with PEDOT:PSS-coated ITO.

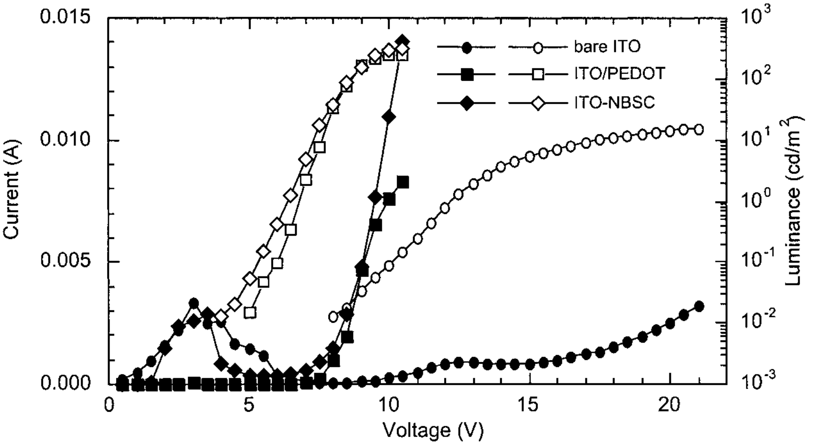

Figure 6. Current (filled symbols) and luminance of LEDs based on the PFO:PFTSO2 blend (80 nm thick).

Acknowledgment

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[1] Y. Cao, G. Yu, C. Zhang, R. Menon, A.J. Heeger, *Synth. Met.* **1997**, *87*, 171.
[2] P.K.H. Ho, J.S. Kim, J.H. Burroughes, H. Becker, S.F.Y. Li, T.M. Brown, F. Cacialli, R.H. Friend, *Nature* **2000**, *404*, 481.
[3] F. Nüesch, L. Si-Ahmed, B. François, L. Zuppiroli, *Adv. Mater.* **1997**, *9*, 222.
[4] S.F.J. Appleyard, S.R. Day, R.D. Pickford, M.R. Wills, *J. Mater. Chem.* **2000**, *10*, 169.
[5] C. Ganzorig, K.-J. Kwak, K. Yagi, M. Fujihira, *Appl. Phys. Lett.* **2001**, *79*, 272.
[6] B. Choi, J. Rhee, H.H. Lee, *Appl. Phys. Lett.* **2001**, *79*, 2109.
[7] J. Morgado, A. Charas, N. Barbagallo, *Appl. Phys. Lett.* **2002**, *81*, 933.
[8] M.T. Bernius, M. Inbasekaran, J. O'Brien, W. Wu, *Adv. Mater.* **2000**, *12*, 1737.
[9] H.G. Gilch, W.L. Weelwright, *J. Polym. Sci., Part A-1* **1966**, *4*, 1337.
[10] A. Charas, J. Morgado, J.M.G. Martinho, L. Alcácer, S.F. Lim, R.H. Friend, F. Cacialli, *Polymer*, in press.
[11] A.J. Campbell, D.D.C. Bradley, H. Antoniadis, *J. Appl. Phys.* **2001**, *89*, 3343.
[12] J.S. Kim, B. Lägel, E. Moons, N. Johansson, I.D. Baikie, W.R. Salaneck, R.H. Friend, F. Cacialli, *Synth. Met.* **2000**, *111-112*, 311.
[13] T.M. Brown, J.S. Kim, R.H. Friend, F. Cacialli, R. Daik, W.J. Feast, *Appl. Phys. Lett.* **1999**, *75*, 1679.
[14] A. Charas, J. Morgado, J.M.G. Martinho, A. Fedorov, L. Alcácer, F. Cacialli, *J. Mater. Chem.* **2002**, *12*, 3523.